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(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 944 125 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:  
22.09.1999 Bulletin 1999/38

(51) Int. Cl.<sup>6</sup>: H01M 4/48, H01M 10/40,  
C01G 51/00, C01G 53/00,  
H01M 4/52

(21) Application number: 99104100.5

(22) Date of filing: 18.03.1999

(84) Designated Contracting States:  
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE  
Designated Extension States:  
AL LT LV MK RO SI

(30) Priority: 19.03.1998 JP 9273498

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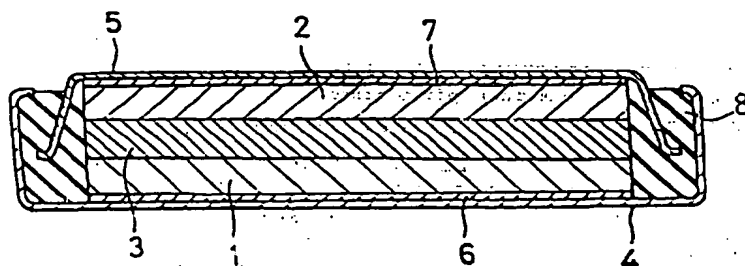
(54) Positive electrode material for lithium secondary battery

(57) A positive electrode (1) active material for a lithium secondary battery including a composite oxide powder having a median diameter of 3.0 through 20.0  $\mu\text{m}$  and a content of particles with a grain size of 1  $\mu\text{m}$  or less of 10% by volume or less and being represented by a composition formula,  $\text{Li}_a\text{Co}_b\text{M}_c\text{Ni}_{1-b-c}\text{O}_2$ , in which M is at least one element selected from the group con-

sisting of B, Mg, Al, Si, Ca, Sc, Ti, V, Cr, Mn, Fe, Cu, Zn, Ga, Ge, Y Nb, Mo, Ru, Rh, Pd, Ag, Cd, In and Sn;  $0 \leq a \leq 1.2$ ;  $0.01 \leq b \leq 0.4$ ;  $0.01 \leq c \leq 0.4$ ; and  $0.02 \leq b+c \leq 0.5$ . Thus, the lithium secondary battery can be improved in its charge-discharge cycle characteristic.

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## Description

[0001] This application claims the priority of Japanese Patent Application No. 10-92734 filed on March 19, 1998, which is incorporated herein by reference.

[0002] The present invention relates to a lithium secondary battery, and more particularly, it relates to improvement of a positive electrode active material used therein for the purpose of providing a lithium secondary battery with an excellent charge-discharge cycle characteristic.

[0003] A lithium secondary battery can be improved in its voltage and capacity by appropriately selecting a positive electrode material because there is no need to consider a water decomposition voltage. Therefore, in accordance with recent development of portable and/or cordless electronic equipment, lithium secondary batteries have been regarded as a promising driving power supply for such electronic equipment.

[0004] Lithium cobaltite ( $\text{LiCoO}_2$ ) has already been practically used as a positive electrode active material in a lithium secondary battery, and the use results in a battery with a high energy density and a high discharge voltage of the 4-V class. Cobalt, that is, a raw material of lithium cobaltite, is, however, a scarce resource and expensive, and hence, use of lithium nickelate ( $\text{LiNiO}_2$ ) in place of lithium cobaltite is now under examination.

[0005] Lithium nickelate has, however, a disadvantage that the capacity of a battery including this material is largely degraded through charge-discharge cycles because its crystal structure is less stable than that of lithium cobaltite.

[0006] As a positive electrode active material usable for overcoming this problem, a composite oxide obtained by substituting part of nickel atoms included in lithium nickelate with cobalt atoms and manganese atoms is reported (see Japanese Laid-Open Patent Publication No. 8-37007/1996). However, the stability, during charge-discharge cycles, of the crystal structure of this composite oxide is still not sufficient to be used in place of lithium cobaltite.

[0007] In consideration of the aforementioned conventional disadvantages, an object of the invention is providing a lithium secondary battery having an excellent charge-discharge characteristic. This object can be achieved by utilizing a specific positive electrode active material as follows:

[0008] The lithium secondary battery of this invention comprises, as a positive electrode active material, a composite oxide powder having a median diameter of 3.0 through 20.0  $\mu\text{m}$  and a content of particles with a grain size of 1  $\mu\text{m}$  or less of 10% by volume or less and being represented by a composition formula,  $\text{Li}_a\text{Co}_b\text{M}_c\text{Ni}_{1-b-c}\text{O}_2$ , in which M is at least one element selected from the group consisting of B, Mg, Al, Si, Ca, Sc, Ti, V, Cr, Mn, Fe, Cu, Zn, Ga, Ge, Y, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In and Sn;  $0 \leq a \leq 1.2$ ;  $0.01 \leq b \leq 0.4$ ;  $0.01 \leq c \leq 0.4$ ; and  $0.02 \leq b+c \leq 0.5$ .

[0009] Alternatively, the lithium secondary battery of this invention comprises, as a positive electrode active material, a composite oxide powder having a median diameter of 6.0 through 15.0  $\mu\text{m}$  and a content of particles with a grain size of 1  $\mu\text{m}$  or less of 10% by volume or less and being represented by a composition formula,  $\text{Li}_a\text{Co}_b\text{M}_c\text{Ni}_{1-b-c}\text{O}_2$ , in which M is at least one element selected from the group consisting of B, Mg, Al, Si, Ca, Sc, Ti, V, Cr, Mn, Fe, Cu, Zn, Ga, Ge, Y, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In and Sn;  $0 \leq a \leq 1.2$ ;  $0.01 \leq b \leq 0.4$ ;  $0.01 \leq c \leq 0.4$ ; and  $0.02 \leq b+c \leq 0.5$ .

[0010] Alternatively, the lithium secondary battery of this invention comprises, as a positive electrode active material, a composite oxide powder having a median diameter of 3.0 through 20.0  $\mu\text{m}$  and a content of particles with a grain size of 1  $\mu\text{m}$  or less of 10% by volume or less and being represented by a composition formula,  $\text{Li}_a\text{Co}_b\text{M}_c\text{Ni}_{1-b-c}\text{O}_2$ , in which M is at least one element selected from the group consisting of B, Mg, Al, Ca, Ti, V, Mn, Fe, Cu, Zn and Ga;  $0 \leq a \leq 1.2$ ;  $0.01 \leq b \leq 0.4$ ;  $0.01 \leq c \leq 0.4$ ; and  $0.02 \leq b+c \leq 0.5$ .

[0011] Alternatively, the lithium secondary battery of this invention comprises, as a positive electrode active material, a composite oxide powder having a median diameter of 6.0 through 15.0  $\mu\text{m}$  and a content of particles with a grain size of 1  $\mu\text{m}$  or less of 10% by volume or less and being represented by a composition formula,  $\text{Li}_a\text{Co}_b\text{M}_c\text{Ni}_{1-b-c}\text{O}_2$ , in which M is at least one element selected from the group consisting of B, Mg, Al, Ca, Ti, V, Mn, Fe, Cu, Zn and Ga;  $0 \leq a \leq 1.2$ ;  $0.01 \leq b \leq 0.4$ ;  $0.01 \leq c \leq 0.4$ ; and  $0.02 \leq b+c \leq 0.5$ .

[0012] Owing to these features of the composite oxide powder according to the invention, a lithium secondary battery having an excellent charge-discharge cycle characteristic can be obtained.

[0013] A more complete appreciation of the invention and many of the attendant advantages thereof will be readily obtained as the same become better understood by reference to the following detailed description when considered in connection with the accompanying drawings; wherein:

Figure 1 is a sectional view of a lithium secondary battery manufactured in an experiment of the invention.

[0014] A lithium secondary battery according to the invention comprises, as a positive electrode active material, a composite oxide powder having a median diameter of 3.0 through 20.0  $\mu\text{m}$  and a content of particles with a grain size of 1  $\mu\text{m}$  or less of 10% by volume or less and represented by a composition formula,  $\text{Li}_a\text{Co}_b\text{M}_c\text{Ni}_{1-b-c}\text{O}_2$ , in which M indicates at least one element selected from the group consisting of B, Mg, Al, Si, Ca, Sc, Ti, V, Cr, Mn, Fe, Cu, Zn, Ga, Ge, Y, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In and Sn;  $0 \leq a \leq 1.2$ ;  $0.01 \leq b \leq 0.4$ ;  $0.01 \leq c \leq 0.4$ ; and  $0.02 \leq b+c \leq 0.5$ . A median diameter is a grain size attained at frequency of 50% on a frequency curve, and is used as a kind of average grain sizes.

[0015] The composite oxide powder having the aforementioned composition is used in this invention because this composite oxide powder is less degraded in its crystal structure through repeated occlusion and discharge of lithium ions during charge-discharge cycles. A composite oxide powder represented by a composition formula,  $\text{Li}_x\text{Co}_y\text{M}_z\text{Ni}_{1-x-y-z}\text{O}_2$ , in which M indicates at least one element selected from the group consisting of B, Mg, Al, Ca, Ti, V, Mn, Fe, Cu, Zn and Ga;  $0 \leq a \leq 1.2$ ;  $0.01 \leq b \leq 0.4$ ;  $0.01 \leq c \leq 0.4$ ; and  $0.02 \leq b+c \leq 0.5$ , is more preferred because its crystal structure is further less degraded during charge-discharge cycles.

[0016] The median diameter of the composite oxide powder is specified to 3.0 through 20.0  $\mu\text{m}$  for the following reasons: When the median diameter is smaller than 3.0  $\mu\text{m}$ , the total surface area of the powder is too large to easily react with an electrolyte solution. As a result, a decomposition product of the electrolyte solution is deposited on the particle surfaces of the positive electrode active material, thereby abruptly decreasing the discharge capacity during charge-discharge cycles. On the other hand, when the median diameter exceeds 20.0  $\mu\text{m}$ , the total surface area of the powder is so small that the lithium ions are occluded and discharged in merely a small area during charge-discharge cycles. As a result, the positive electrode active material is abruptly degraded during charge-discharge cycles. More preferably, the composite oxide powder has a median diameter of 6.0 through 15.0  $\mu\text{m}$ .

[0017] The content of the particles with a grain size of 1  $\mu\text{m}$  or less in the composite oxide powder is specified to 10% by volume or less for the following reason: When the content of the fine particles with a grain size of 1  $\mu\text{m}$  or less exceeds 10% by volume, the total surface area of the powder is too large to easily react with the electrolyte solution. As a result, the decomposition product of the electrolyte solution is deposited on the particle surfaces of the composite oxide, thereby abruptly decreasing the discharge capacity during charge-discharge cycles.

[0018] The composite oxide powder preferably has a specific surface area measured by a BET method of 0.15 through 2.00  $\text{m}^2/\text{g}$  because a lithium secondary battery with an excellent charge-discharge cycle characteristic can be obtained by using such a powder.

[0019] The present invention relates to improvement of a positive electrode active material for the purpose of providing a lithium secondary battery with a good charge-discharge cycle characteristic. Accordingly, materials for other members such as a negative electrode and an electrolyte solution can be any of various materials practically used or proposed as materials for conventional lithium secondary batteries.

[0020] Examples of the negative electrode material include a material capable of electrochemically occluding and discharging lithium ions and metallic lithium. Examples of the material capable of electrochemically occluding and discharging lithium ions include carbon materials such as graphite (including natural graphite and artificial graphite), coke and an organic baked substance; lithium alloys such as lithium-aluminum alloy, lithium-magnesium alloy, lithium-indium alloy, lithium-tin alloy, lithium-thallium alloy, lithium-lead alloy and lithium-bismuth alloy; and metal oxides and metal sulfides including one of or two or more of tin, titanium, iron, molybdenum, niobium, vanadium and zinc.

[0021] An example of the electrolyte solution includes a solution obtained by dissolving an electrolytic salt such as  $\text{LiPF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiCF}_3\text{SO}_3$  and  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  in an organic solvent such as ethylene carbonate, propylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, methyl ethyl carbonate,  $\gamma$ -butyrolactone, sulfolane, 1,2-dimethoxyethane, 1,2-diethoxyethane, 1,2-ethoxymethoxyethane, tetrahydrofuran, 2-methyl-1,3-dioxolane, 4-methyl-1,3-dioxolane, dimethyl ether and diethyl ether, in a concentration of 0.7 through 1.5 moles per liter.

[0022] Other features of the invention will become more apparent in the course of the following descriptions of exemplary embodiments which are given for illustration of the invention and not intended to be limiting thereof.

## Experiment 1

[0023] The relationship between the composition of a positive electrode active material and the charge-discharge cycle characteristic was examined as follows:

### Preparation of positive electrodes:

[0024] Lithium hydroxide ( $\text{LiOH}$ ), nickel hydroxide ( $\text{Ni}(\text{OH})_2$ ), cobalt hydroxide ( $\text{Co}(\text{OH})_2$ ) and manganese dioxide ( $\text{MnO}_2$ ) were mixed in various ratios in mortars, and the resultant mixtures were baked in an atmosphere of oxygen at a temperature of 750°C for 20 hours. In this manner, sixteen kinds of composite oxides each in the form of a mass were obtained.

[0025] Each of the composite oxides was crushed by using a jet mill, thereby preparing a composite oxide powder to be used as a positive electrode active material. Table 1 lists the following features of each composite oxide: An atomic ratio among respective elements (i.e., Li:Ni:Co:Mn), a median diameter (in  $\mu\text{m}$ ), a content of particles with a grain size of 1  $\mu\text{m}$  or less (in % by volume), and a specific surface area measured by the BET method (in  $\text{m}^2/\text{g}$ ). The median diameter was obtained through laser diffraction. Also, helium was used as an absorbed substance in the BET method.

Table 1

| Battery         | Atomic ratio of elements in composite oxide |      |      |      | Median diameter ( $\mu\text{m}$ ) | Content of particles with size of 1 $\mu\text{m}$ or less (%) by volume | Specific surface area ( $\text{m}^2/\text{g}$ ) | Charge-discharge cycles |
|-----------------|---|------|------|------|-----------------------------------|---|---|-------------------------|
|                 | Li  | Ni   | Co   | Mn   |                                   |   |   |                         |
| A1 (invention)  | 1.00  | 0.98 | 0.01 | 0.01 | 10.3                              | 9.5   | 1.32  | 325                     |
| A2 (invention)  | 1.00  | 0.79 | 0.01 | 0.20 | 10.5                              | 9.2   | 1.51  | 332                     |
| A3 (invention)  | 1.00  | 0.59 | 0.01 | 0.40 | 9.7                               | 9.2   | 1.15  | 340                     |
| A4 (invention)  | 1.00  | 0.50 | 0.10 | 0.40 | 10.0                              | 9.3   | 1.12  | 329                     |
| A5 (invention)  | 1.00  | 0.79 | 0.20 | 0.01 | 10.9                              | 8.9   | 1.26  | 330                     |
| A6 (invention)  | 1.00  | 0.60 | 0.20 | 0.20 | 10.3                              | 9.0   | 0.98  | 329                     |
| A7 (invention)  | 1.00  | 0.50 | 0.20 | 0.30 | 9.6                               | 9.6   | 1.01  | 327                     |
| A8 (invention)  | 1.00  | 0.59 | 0.40 | 0.01 | 10.2                              | 8.9   | 1.22  | 325                     |
| A9 (invention)  | 1.00  | 0.50 | 0.40 | 0.10 | 11.0                              | 8.8   | 1.18  | 331                     |
| B1 (comparison) | 1.00  | 0.50 | 0.45 | 0.05 | 9.2                               | 9.2   | 1.54  | 159                     |
| B2 (comparison) | 1.00  | 0.50 | 0.05 | 0.45 | 9.5                               | 9.7   | 1.25  | 157                     |
| B3 (comparison) | 1.00  | 0.45 | 0.15 | 0.40 | 10.1                              | 9.6   | 0.86  | 160                     |
| B4 (comparison) | 1.00  | 0.45 | 0.40 | 0.15 | 10.7                              | 9.5   | 1.23  | 162                     |
| B5 (comparison) | 1.00  | 0.90 | 0.00 | 0.10 | 9.9                               | 9.4   | 0.94  | 103                     |
| B6 (comparison) | 1.00  | 0.90 | 0.10 | 0.00 | 10.6                              | 9.0   | 1.16  | 110                     |
| B7 (comparison) | 1.00  | 1.00 | 0.00 | 0.00 | 9.8                               | 8.9   | 1.04  | 57                      |

[0026] Each of the composite oxide powders, acetylene black serving as a conducting agent and poly(vinylidene fluoride) serving as a binder were mixed in a ratio by weight of 90:6:4 and kneaded to give a positive electrode mixed material. The positive electrode mixed material was pressed at a pressure of 2 ton/cm<sup>2</sup>, so as to be formed into a disk with a diameter of 20 mm. The resultant disk was heat-treated under vacuum at a temperature of 250°C for 2 hours. Thus, the positive electrode of each battery was prepared.

#### Preparation of negative electrode:

[0027] A negative electrode was prepared by punching a rolled plate of lithium-aluminum alloy into a disk with a diameter of 20 mm.

#### Preparation of electrolyte solution:

[0028] An electrolyte solution was prepared by dissolving LiPF<sub>6</sub> in a mixed solvent including ethylene carbonate and dimethyl carbonate in a ratio by volume of 1:1.

Manufacture of batteries:

[0029] Flat type lithium secondary batteries (i.e., batteries A1 through A9 according to the invention and comparative batteries B1 through B7) were manufactured by using the aforementioned positive and negative electrodes and electrolyte solution. Figure 1 is a sectional view of the lithium secondary battery. The lithium secondary battery BA of Figure 1 comprises a positive electrode 1, a negative electrode 2, a separator 3 for separating the positive and negative electrodes, a positive electrode can 4, a negative electrode can 5, a positive electrode collector 6, a negative electrode collector 7 and an insulating packing 8. The positive electrode 1 and the negative electrode 2, opposing each other with the separator 3 impregnated with the electrolyte solution sandwiched therebetween, are housed in a battery can formed by the positive and negative electrode cans 4 and 5. The positive electrode 1 is connected with the positive electrode can 4 through the positive electrode collector 6 and the negative electrode 2 is connected with the negative electrode can 5 through the negative electrode collector 7, so that a chemical energy generated within the battery can be taken out as an electric energy.

Charge-discharge cycle test:

[0030] Each battery was subjected to a charge-discharge cycle test, in which the battery was charged at a current density of 0.5 mA/cm<sup>2</sup> to 4.25 V and discharged at a current density of 0.5 mA/cm<sup>2</sup> to 2.75V in each cycle. In this manner, the number of charge-discharge cycles repeated until the discharge capacity became smaller than 90% of that in the first cycle was obtained with regard to each battery. The thus obtained numbers of charge-discharge cycles are also shown in Table 1 above.

[0031] It is understood from Table 1 that the present batteries A1 through A9 have remarkably better charge-discharge cycle characteristics than the comparative batteries B1 through B7. This is because the composite oxides used in the present batteries A1 through A9 are more stable in their crystal structures during charge-discharge cycles than the composite oxides used in the comparative batteries B1 through B7.

Experiment 2:

[0032] Lithium hydroxide, nickel hydroxide, cobalt hydroxide and an M material shown in Table 2 (namely, selected from the group consisting of B, Mg, Al, Si, Ca, Sc, Ti, V, Cr, Fe, Cu, Zn, Ga, Ge, Y, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In and Sn) were mixed in a mortar in an atomic ratio of Li:Ni:Co:M of 1.0:0.6:0.3:0.1, and the resultant mixture was baked in an atmosphere of oxygen at a temperature of 750°C for 20 hours. Thus, twenty four kinds of composite oxides each in the form of a mass were obtained.

[0033] Each of the composite oxides was crushed by using a jet mill, thereby preparing a composite oxide powder. Table 2 also lists a median diameter (in  $\mu\text{m}$ ), a content of particles with a grain size of 1  $\mu\text{m}$  or less (in % by volume) and a specific surface area (in m<sup>2</sup>/g) measured by the BET method of each composite oxide powder.

Table 2

| Battery         | Material of M                  | Median diameter ( $\mu\text{m}$ ) | Content of particles with size of 1 $\mu\text{m}$ or less (% by volume) | Specific surface area (m <sup>2</sup> /g) | Charge-discharge cycles |
|-----------------|--------------------------------|-----------------------------------|---|---|-------------------------|
| A10 (invention) | H <sub>3</sub> BO <sub>3</sub> | 10.2                              | 9.7   | 1.55                                      | 330                     |
| A11 (invention) | Mg(OH) <sub>2</sub>            | 11.0                              | 9.4   | 0.93                                      | 328                     |
| A12 (invention) | Al(OH) <sub>3</sub>            | 9.8                               | 8.9   | 1.26                                      | 342                     |
| A13 (invention) | SiO                            | 9.7                               | 9.6   | 1.07                                      | 312                     |
| A14 (invention) | Ca(OH) <sub>2</sub>            | 10.9                              | 10.2  | 1.32                                      | 325                     |
| A15 (invention) | Sc <sub>2</sub> O <sub>3</sub> | 10.5                              | 10.7  | 1.23                                      | 308                     |
| A16 (invention) | Ti(OH) <sub>4</sub>            | 9.5                               | 9.7   | 0.84                                      | 330                     |
| A17 (invention) | V <sub>2</sub> O <sub>5</sub>  | 10.1                              | 10.1  | 1.01                                      | 331                     |
| A18 (invention) | Cr <sub>2</sub> O <sub>3</sub> | 9.9                               | 10.0  | 0.93                                      | 310                     |
| A19 (invention) | FeOOH                          | 10.7                              | 9.7   | 1.15                                      | 339                     |

Table 2 (cont)

| Battery         | Material of M            | Median diameter ( $\mu\text{m}$ ) | Content of particles with size of 1 $\mu\text{m}$ or less (% by volume) | Specific surface area ( $\text{m}^2/\text{g}$ ) | Charge-discharge cycles |
|-----------------|--------------------------|-----------------------------------|---|---|-------------------------|
| A20 (invention) | $\text{Cu}(\text{OH})_2$ | 10.4                              | 11.2  | 0.96  | 328                     |
| A21 (invention) | $\text{ZnO}$             | 11.0                              | 10.7  | 1.24  | 330                     |
| A22 (invention) | $\text{Ca}_2\text{O}_3$  | 9.5                               | 10.4  | 1.27  | 329                     |
| A23 (invention) | $\text{GeO}_2$           | 10.4                              | 9.7   | 1.38  | 305                     |
| A24 (invention) | $\text{Y}_2\text{O}_3$   | 10.3                              | 8.8   | 0.75  | 301                     |
| A25 (invention) | $\text{Nb}_2\text{O}_5$  | 9.7                               | 10.2  | 1.54  | 309                     |
| A26 (invention) | $\text{MoO}_2$           | 10.0                              | 10.3  | 1.33  | 302                     |
| A27 (invention) | $\text{RuO}_2$           | 10.1                              | 10.9  | 0.84  | 304                     |
| A28 (invention) | $\text{Rh}_2\text{O}_3$  | 9.9                               | 10.7  | 1.45  | 305                     |
| A29 (invention) | $\text{PdO}$             | 9.7                               | 9.7   | 1.22  | 310                     |
| A30 (invention) | $\text{Ag}_2\text{O}$    | 11.0                              | 10.4  | 0.74  | 301                     |
| A31 (invention) | $\text{Cd}(\text{OH})_2$ | 10.7                              | 9.9   | 1.63  | 302                     |
| A32 (invention) | $\text{In}_2\text{O}_3$  | 10.4                              | 10.0  | 1.31  | 301                     |
| A33 (invention) | $\text{SnO}$             | 9.7                               | 9.6   | 1.77  | 304                     |

[0034] Lithium secondary batteries (i.e., present batteries A10 through A33) were manufactured in the same manner as in Experiment 1 except that the aforementioned composite oxide powders were used as the positive electrode active materials for the respective batteries. These batteries were subjected to the charge-discharge cycle test under the same conditions as in Experiment 1, and the obtained numbers of charge-discharge cycles are also shown in Table 2 above.

[0035] It is understood from Table 2 that the element M partially substituted in Ni for improving the stability of the composite oxide in charge-discharge cycles can be not only Mn but also B, Mg, Al, Si, Ca, Sc, Ti, V, Cr, Fe, Cu, Zn, Ga, Ge, Y, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In and Sn. Also, it is understood from Tables 1 and 2 that B, Mg, Al, Ca, Ti, V, Mn, Fe, Cu, Zn and Ga are more preferably used as the element M partially substituted in Ni.

### Experiment 3

[0036] Lithium hydroxide, nickel hydroxide, cobalt hydroxide and manganese dioxide were mixed in a mortar in an atomic ratio of Li:Ni:Co:Mn of 1.0:0.6:0.3:0.1, and the resultant mixture was baked in an atmosphere of oxygen at a temperature of 750°C for 20 hours. Thus, a composite oxide in the form of a mass represented by a composition formula of  $\text{LiNi}_{0.6}\text{Co}_{0.3}\text{Mn}_{0.1}\text{O}_2$  was obtained.

[0037] This composite oxide was crushed by using a jet mill under various conditions, thereby preparing nine kinds of composite oxide powders. The median diameter, the content of particles with a grain size of 1  $\mu\text{m}$  or less (in % by volume) and the specific surface area (in  $\text{m}^2/\text{g}$ ) of each of the composite oxide powders are shown in Table 3.

Table 3

| Battery         | Median diameter ( $\mu\text{m}$ ) | Content of particles with size of 1 $\mu\text{m}$ or less (% by volume) | Specific surface area ( $\text{m}^2/\text{g}$ ) | Charge-discharge cycles |
|-----------------|-----------------------------------|---|---|-------------------------|
| A34 (invention) | 3.0                               | 10.0  | 1.99  | 301                     |
| A35 (invention) | 6.0                               | 10.0  | 1.72  | 329                     |
| A36 (invention) | 12.5                              | 8.2   | 1.55  | 332                     |



Table 3 (continued)

| Battery          | Median diameter ( $\mu\text{m}$ ) | Content of particles with size of $1\ \mu\text{m}$ or less (% by volume) | Specific surface area ( $\text{m}^2/\text{g}$ ) | Charge-discharge cycles |
|------------------|-----------------------------------|--|---|-------------------------|
| A37 (invention)  | 15.0                              | 5.5  | 1.34  | 335                     |
| A38 (invention)  | 20.0                              | 2.1  | 1.27  | 302                     |
| B8 (comparison)  | 2.2                               | 10.0   | 1.97  | 195                     |
| B9 (comparison)  | 21.4                              | 0.5  | 0.74  | 182                     |
| B10 (comparison) | 12.6                              | 10.5   | 1.18  | 173                     |
| B11 (comparison) | 10.5                              | 12.0   | 1.24  | 165                     |

[0038] Lithium secondary batteries (i.e., present batteries A34 through A38 and comparative batteries B8 through B11) were manufactured in the same manner as in Experiment 1 except that the aforementioned composite oxide powders were used as the positive electrode active materials for the respective batteries. These batteries were subjected to the charge-discharge cycle test under the same conditions as in Experiment 1. The thus obtained numbers of charge-discharge cycles are also shown in Table 3 above.

[0039] It is understood from Table 3 that the present batteries A34 through A38, each of which has a median diameter of  $3.0$  through  $20.0\ \mu\text{m}$  and a content of particles with a grain size of  $1\ \mu\text{m}$  or less of  $10\%$  by volume or less, have better charge-discharge cycle characteristics than the comparative batteries B8 through B11, in which the median diameter or the content of particles with a grain size of  $1\ \mu\text{m}$  or less does not fall within the range herein specified. Also, as is shown in Table 3, among the present batteries A34 through A38, the batteries A35 through A37 have particularly good charge-discharge cycle characteristics. Therefore, it is understood that a composite oxide with a median diameter of  $6.0$  through  $15.0\ \mu\text{m}$  is more preferred.

#### Experiment 4:

[0040] Lithium hydroxide, nickel hydroxide, cobalt hydroxide and manganese dioxide were mixed in a mortar in an atomic ratio of Li:Ni:Co:Mn of  $1.0:0.6:0.3:0.1$ , and the resultant mixture was baked in an atmosphere of oxygen at a temperature of  $750^\circ\text{C}$  for 20 hours. Thus, a composite oxide in the form of a mass represented by a composition formula of  $\text{LiNi}_{0.6}\text{Co}_{0.3}\text{Mn}_{0.1}\text{O}_2$  was obtained. At this point, the grain sizes of the materials to be used were variously changed so as to adjust the shapes of the resultant composite oxides and pores included therein. Thus, eighteen kinds of composite oxides, each in the form of a mass, different from one another in the median diameter or the specific surface area were obtained.

[0041] Each of the thus obtained composite oxides was crushed by using a jet mill, thereby preparing a composite oxide powder. Table 4 lists the median diameter, the content of particles with a grain size of  $1\ \mu\text{m}$  or less (in % by volume) and the specific surface area measured by the BET method of each composite oxide powder.

Table 4

| Battery         | Median diameter ( $\mu\text{m}$ ) | Content of particles with size of $1\ \mu\text{m}$ or less (% by volume) | Specific surface area ( $\text{m}^2/\text{g}$ ) | Charge-discharge cycles |
|-----------------|-----------------------------------|--|---|-------------------------|
| A39 (invention) | 3.0                               | 9.9  | 2.00  | 301                     |
| A40 (invention) | 3.0                               | 10.0   | 2.12  | 275                     |
| A41 (invention) | 6.0                               | 3.2  | 0.12  | 304                     |
| A42 (invention) | 6.0                               | 9.8  | 0.15  | 325                     |
| A35 (invention) | 6.0                               | 10.0   | 1.72  | 329                     |
| A43 (invention) | 6.0                               | 9.7  | 2.00  | 325                     |
| A44 (invention) | 6.0                               | 9.9  | 2.05  | 300                     |
| A45 (invention) | 12.5                              | 3.9  | 0.13  | 297                     |

Table 4 (continued)

| Battery         | Median diameter ( $\mu\text{m}$ ) | Content of particles with size of 1 $\mu\text{m}$ or less (% by volume) | Specific surface area ( $\text{m}^2/\text{g}$ ) | Charge-discharge cycles |
|-----------------|-----------------------------------|---|---|-------------------------|
| A46 (invention) | 12.5                              | 4.2   | 0.15  | 330                     |
| A36 (invention) | 12.5                              | 8.2   | 1.55  | 332                     |
| A47 (invention) | 12.5                              | 8.9   | 2.00  | 323                     |
| A48 (invention) | 12.5                              | 9.2   | 2.09  | 302                     |
| A49 (invention) | 15.0                              | 3.1   | 0.13  | 296                     |
| A50 (invention) | 15.0                              | 4.5   | 0.15  | 342                     |
| A37 (invention) | 15.0                              | 5.5   | 1.34  | 335                     |
| A51 (invention) | 15.0                              | 9.5   | 2.00  | 325                     |
| A52 (invention) | 15.0                              | 9.7   | 2.05  | 299                     |
| A53 (invention) | 20.0                              | 0.5   | 0.13  | 270                     |
| A54 (invention) | 20.0                              | 0.8   | 0.15  | 298                     |
| A38 (invention) | 20.0                              | 2.1   | 1.27  | 302                     |
| A55 (invention) | 20.0                              | 3.2   | 2.00  | 305                     |
| A56 (invention) | 20.0                              | 4.3   | 2.09  | 267                     |

[0042] Lithium secondary batteries (i.e., present batteries A39 through A56) were manufactured in the same manner as in Experiment 1 except that the aforementioned composite oxide powders were used as the positive electrode active materials for the respective batteries. The respective batteries were subjected to the charge-discharge cycle test under the same conditions as in Experiment 1, and the results are also shown in Table 4 above. It is noted that Table 4 also lists the results obtained in the present batteries A35 through A38 shown in Table 3 for comparison.

[0043] On the basis of comparison in Table 4 between the present battery A39 and the present battery A40, between the present batteries A35, A42 and A43 and the present batteries A41 and A44, between the present batteries A36, A46 and A47 and the present batteries A45 and A48, between the present batteries A37, A50 and A51 and the present batteries A49 and A52, and between the present batteries A38, A54 and A55 and the present batteries A53 and A56, it is understood that a lithium secondary battery having an excellent charge-discharge cycle characteristic can be obtained when the composite oxide powder has a specific surface area measured by the BET method of 0.15 through 2.00  $\text{m}^2/\text{g}$ .

[0044] Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described herein.

#### Claims

1. A lithium secondary battery comprising, as a positive electrode active material, a composite oxide powder having a median diameter of 3.0 through 20.0  $\mu\text{m}$  and a content of particles with a grain size of 1  $\mu\text{m}$  or less of 10% by volume or less and being represented by a composition formula,  $\text{Li}_a\text{Co}_b\text{M}_c\text{Ni}_{1-b-c}\text{O}_2$ , in which M is at least one element selected from the group consisting of B, Mg, Al, Si, Ca, Sc, Ti, V, Cr, Mn, Fe, Cu, Zn, Ga, Ge, Y, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In and Sn;  $0 \leq a \leq 1.2$ ;  $0.01 \leq b \leq 0.4$ ;  $0.01 \leq c \leq 0.4$  and  $0.02 \leq b+c \leq 0.5$ .
2. A lithium secondary battery comprising, as a positive electrode active material, a composite oxide powder having a median diameter of 6.0 through 15.0  $\mu\text{m}$  and a content of particles with a grain size of 1  $\mu\text{m}$  or less of 10% by volume or less and being represented by a composition formula,  $\text{Li}_a\text{Co}_b\text{M}_c\text{Ni}_{1-b-c}\text{O}_2$ , in which M is at least one element selected from the group consisting of B, Mg, Al, Si, Ca, Sc, Ti, V, Cr, Mn, Fe, Cu, Zn, Ga, Ge, Y, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In and Sn;  $0 \leq a \leq 1.2$ ;  $0.01 \leq b \leq 0.4$ ;  $0.01 \leq c \leq 0.4$ ; and  $0.02 \leq b+c \leq 0.5$ .
3. A lithium secondary battery comprising, as a positive electrode active material, a composite oxide powder having a median diameter of 3.0 through 20.0  $\mu\text{m}$  and a content of particles with a grain size of 1  $\mu\text{m}$  or less of 10% by

volume or less and being represented by a composition formula,  $\text{Li}_a\text{Co}_b\text{M}_c\text{Ni}_{1-b-c}\text{O}_2$ , in which M is at least one element selected from the group consisting of B, Mg, Al, Ca, Ti, V, Mn, Fe, Cu, Zn and Ga;  $0 \leq a \leq 1.2$ ;  $0.01 \leq b \leq 0.4$ ;  $0.01 \leq c \leq 0.4$ ; and  $0.02 \leq b+c \leq 0.5$ .

4. A lithium secondary battery comprising, as a positive electrode active material, a composite oxide powder having a median diameter of 6.0 through 15.0  $\mu\text{m}$  and a content of particles with a grain size of 1  $\mu\text{m}$  or less of 10% by volume or less and being represented by a composition formula,  $\text{Li}_a\text{Co}_b\text{M}_c\text{Ni}_{1-b-c}\text{O}_2$ , in which M is at least one element selected from the group consisting of B, Mg, Al, Ca, Ti, V, Mn, Fe, Cu, Zn and Ga;  $0 \leq a \leq 1.2$ ;  $0.01 \leq b \leq 0.4$ ;  $0.01 \leq c \leq 0.4$ ; and  $0.02 \leq b+c \leq 0.5$ .

5. The lithium secondary battery according to Claim 1, 2, 3 or 4, wherein the composite oxide powder has a specific surface area measured by a BET method of 0.15 through 2.00  $\text{m}^2/\text{g}$ .

6. A positive electrode active material for a lithium secondary battery comprising a composite oxide powder having a median diameter of 3.0 through 20.0  $\mu\text{m}$  and a content of particles with a grain size of 1  $\mu\text{m}$  or less of 10% by volume or less and being represented by a composition formula,  $\text{Li}_a\text{Co}_b\text{M}_c\text{Ni}_{1-b-c}\text{O}_2$ , in which M is at least one element selected from the group consisting of B, Mg, Al, Si, Ca, Sc, Ti, V, Cr, Mn, Fe, Cu, Zn, Ga, Ge, Y, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In and Sn;  $0 \leq a \leq 1.2$ ;  $0.01 \leq b \leq 0.4$ ;  $0.01 \leq c \leq 0.4$ ; and  $0.02 \leq b+c \leq 0.5$ .

7. A positive electrode active material for a lithium secondary battery comprising a composite oxide powder having a median diameter of 6.0 through 15.0  $\mu\text{m}$  and a content of particles with a grain size of 1  $\mu\text{m}$  or less of 10% by volume or less and being represented by a composition formula,  $\text{Li}_a\text{Co}_b\text{M}_c\text{Ni}_{1-b-c}\text{O}_2$ , in which M is at least one element selected from the group consisting of B, Mg, Al, Si, Ca, Sc, Ti, V, Cr, Mn, Fe, Cu, Zn, Ga, Ge, Y, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In and Sn;  $0 \leq a \leq 1.2$ ;  $0.01 \leq b \leq 0.4$ ;  $0.01 \leq c \leq 0.4$ ; and  $0.02 \leq b+c \leq 0.5$ .

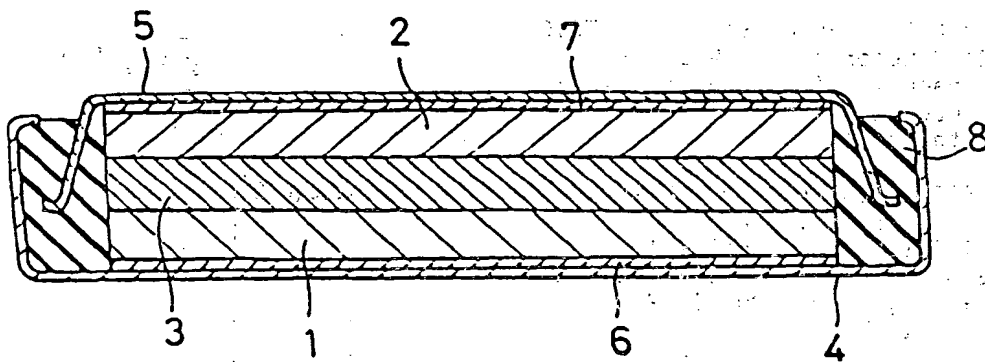
8. A positive electrode active material for a lithium secondary battery comprising a composite oxide powder having a median diameter of 3.0 through 20.0  $\mu\text{m}$  and a content of particles with a grain size of 1  $\mu\text{m}$  or less of 10% by volume or less and being represented by a composition formula,  $\text{Li}_a\text{Co}_b\text{M}_c\text{Ni}_{1-b-c}\text{O}_2$ , in which M is at least one element selected from the group consisting of B, Mg, Al, Ca, Ti, V, Mn, Fe, Cu, Zn and Ga;  $0 \leq a \leq 1.2$ ;  $0.01 \leq b \leq 0.4$ ;  $0.01 \leq c \leq 0.4$ ; and  $0.02 \leq b+c \leq 0.5$ .

9. A positive electrode active material for a lithium secondary battery comprising a composite oxide powder having a median diameter of 6.0 through 15.0  $\mu\text{m}$  and a content of particles with a grain size of 1  $\mu\text{m}$  or less of 10% by volume or less and being represented by a composition formula,  $\text{Li}_a\text{Co}_b\text{M}_c\text{Ni}_{1-b-c}\text{O}_2$ , in which M is at least one element selected from the group consisting of B, Mg, Al, Ca, Ti, V, Mn, Fe, Cu, Zn and Ga;  $0 \leq a \leq 1.2$ ;  $0.01 \leq b \leq 0.4$ ;  $0.01 \leq c \leq 0.4$ ; and  $0.02 \leq b+c \leq 0.5$ .

10. The positive electrode active material for a lithium secondary battery according to Claim 6, 7, 8 or 9, wherein the composite oxide powder has a specific surface area measured by a BET method of 0.15 through 2.00  $\text{m}^2/\text{g}$ .

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## EUROPEAN SEARCH REPORT

Application Number  
EP 99 10 4100

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| -/-   |   |  |   |
| The present search report has been drawn up for all claims  |   |  |   |
| Place of search<br>THE HAGUE  |   | Date of completion of the search<br>22 July 1999 | Examiner<br>Gamez, A  |
| <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone<br/>Y : particularly relevant if combined with another document of the same category<br/>A : technological background<br/>O : non-written disclosure<br/>P : intermediate document</p> <p>T : theory or principle underlying the invention<br/>E : earlier patent document, but published on, or after the filing date<br/>D : document cited in the application<br/>L : document cited for other reasons<br/>&amp; : member of the same patent family, corresponding document</p> |   |  |   |

EPO FORM 1503 03.82 (P04C01)



European Patent  
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# EUROPEAN SEARCH REPORT

Application Number  
EP 99 10 4100

| DOCUMENTS CONSIDERED TO BE RELEVANT  |  |  |  |
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| Category   | Citation of document with indication, where appropriate, of relevant passages  | Relevant to claim  | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
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| The present search report has been drawn up for all claims   |  |  |  |
| Place of search<br><b>THE HAGUE</b>  |  | Date of completion of the search<br><b>22 July 1999</b>  | Examiner<br><b>Gamez, A</b>                  |
| CATEGORY OF CITED DOCUMENTS<br>X : particularly relevant if taken alone<br>Y : particularly relevant if combined with another document of the same category<br>A : technological background<br>O : non-written disclosure<br>P : intermediate document |  | T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br>& : member of the same patent family, corresponding document |  |

EPO FORM 1503 03/82 (P4/C01)

# ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 99 10 4100

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22-07-1999

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EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

1. The first group of people who are interested in the results of the study are the researchers themselves. They want to know if the study was successful in achieving its objectives and if the data collected is reliable and valid.

[illegible]

1. *Chlorophyll a* and *Chlorophyll b* were determined by the method of Arar and Collins (1971).

the 1990s, the number of people in the United States who are 65 years of age or older has increased by 50 percent, and the number of people 75 years of age or older has increased by 100 percent. The number of people 85 years of age or older has increased by 200 percent. The number of people 95 years of age or older has increased by 400 percent. The number of people 100 years of age or older has increased by 1,000 percent. The number of people 105 years of age or older has increased by 2,000 percent. The number of people 110 years of age or older has increased by 4,000 percent. The number of people 115 years of age or older has increased by 8,000 percent. The number of people 120 years of age or older has increased by 16,000 percent. The number of people 125 years of age or older has increased by 32,000 percent. The number of people 130 years of age or older has increased by 64,000 percent. The number of people 135 years of age or older has increased by 128,000 percent. The number of people 140 years of age or older has increased by 256,000 percent. The number of people 145 years of age or older has increased by 512,000 percent. The number of people 150 years of age or older has increased by 1,024,000 percent. The number of people 155 years of age or older has increased by 2,048,000 percent. The number of people 160 years of age or older has increased by 4,096,000 percent. The number of people 165 years of age or older has increased by 8,192,000 percent. The number of people 170 years of age or older has increased by 16,384,000 percent. The number of people 175 years of age or older has increased by 32,768,000 percent. The number of people 180 years of age or older has increased by 65,536,000 percent. The number of people 185 years of age or older has increased by 131,072,000 percent. The number of people 190 years of age or older has increased by 262,144,000 percent. The number of people 195 years of age or older has increased by 524,288,000 percent. The number of people 200 years of age or older has increased by 1,048,576,000 percent. The number of people 205 years of age or older has increased by 2,097,152,000 percent. The number of people 210 years of age or older has increased by 4,194,304,000 percent. The number of people 215 years of age or older has increased by 8,388,608,000 percent. The number of people 220 years of age or older has increased by 16,777,216,000 percent. The number of people 225 years of age or older has increased by 33,554,432,000 percent. The number of people 230 years of age or older has increased by 67,108,864,000 percent. The number of people 235 years of age or older has increased by 134,217,728,000 percent. The number of people 240 years of age or older has increased by 268,435,456,000 percent. The number of people 245 years of age or older has increased by 536,870,912,000 percent. The number of people 250 years of age or older has increased by 1,073,741,824,000 percent. The number of people 255 years of age or older has increased by 2,147,483,648,000 percent. The number of people 260 years of age or older has increased by 4,294,967,296,000 percent. The number of people 265 years of age or older has increased by 8,589,934,592,000 percent. The number of people 270 years of age or older has increased by 17,179,869,184,000 percent. The number of people 275 years of age or older has increased by 34,359,738,368,000 percent. The number of people 280 years of age or older has increased by 68,719,476,736,000 percent. The number of people 285 years of age or older has increased by 137,438,953,472,000 percent. The number of people 290 years of age or older has increased by 274,877,906,944,000 percent. The number of people 295 years of age or older has increased by 549,755,813,888,000 percent. The number of people 300 years of age or older has increased by 1,099,511,627,776,000 percent. The number of people 305 years of age or older has increased by 2,199,023,255,552,000 percent. The number of people 310 years of age or older has increased by 4,398,046,511,104,000 percent. The number of people 315 years of age or older has increased by 8,796,093,022,208,000 percent. The number of people 320 years of age or older has increased by 17,592,186,044,416,000 percent. The number of people 325 years of age or older has increased by 35,184,372,088,832,000 percent. The number of people 330 years of age or older has increased by 70,368,744,177,664,000 percent. The number of people 335 years of age or older has increased by 140,737,488,355,328,000 percent. The number of people 340 years of age or older has increased by 281,474,976,710,656,000 percent. The number of people 345 years of age or older has increased by 562,949,953,421,312,000 percent. The number of people 350 years of age or older has increased by 1,125,899,906,842,624,000 percent. The number of people 355 years of age or older has increased by 2,251,799,813,685,248,000 percent. The number of people 360 years of age or older has increased by 4,503,599,627,370,496,000 percent. The number of people 365 years of age or older has increased by 9,007,199,254,740,992,000 percent. The number of people 370 years of age or older has increased by 18,014,398,509,481,984,000 percent. The number of people 375 years of age or older has increased by 36,028,797,018,963,968,000 percent. The number of people 380 years of age or older has increased by 72,057,594,037,927,936,000 percent. The number of people 385 years of age or older has increased by 144,115,188,075,855,872,000 percent. The number of people 390 years of age or older has increased by 288,230,376,151,711,744,000 percent. The number of people 395 years of age or older has increased by 576,460,752,303,423,488,000 percent. The number of people 400 years of age or older has increased by 1,152,921,504,606,846,976,000 percent. The number of people 405 years of age or older has increased by 2,305,843,009,213,693,952,000 percent. The number of people 410 years of age or older has increased by 4,611,686,018,427,387,904,000 percent. The number of people 415 years of age or older has increased by 9,223,372,036,854,775,808,000 percent. The number of people 420 years of age or older has increased by 18,446,744,073,709,551,616,000 percent. The number of people 425 years of age or older has increased by 36,893,488,147,419,103,232,000 percent. The number of people 430 years of age or older has increased by 73,786,976,294,838,206,464,000 percent. The number of people 435 years of age or older has increased by 147,573,952,589,676,412,928,000 percent. The number of people 440 years of age or older has increased by 295,147,905,179,352,825,856,000 percent. The number of people 445 years of age or older has increased by 590,295,810,358,705,651,712,000 percent. The number of people 450 years of age or older has increased by 1,180,591,620,717,411,303,424,000 percent. The number of people 455 years of age or older has increased by 2,361,183,241,434,822,606,848,000 percent. The number of people 460 years of age or older has increased by 4,722,366,482,869,645,213,696,000 percent. The number of people 465 years of age or older has increased by 9,444,732,965,739,290,427,392,000 percent. The number of people 470 years of age or older has increased by 18,889,465,931,478,580,854,784,000 percent. The number of people 475 years of age or older has increased by 37,778,931,862,957,161,709,568,000 percent. The number of people 480 years of age or older has increased by 75,557,863,725,914,323,419,136,000 percent. The number of people 485 years of age or older has increased by 151,115,727,451,828,646,838,272,000 percent. The number of people 490 years of age or older has increased by 302,231,454,903,657,293,676,544,000 percent. The number of people 495 years of age or older has increased by 604,462,909,807,314,587,353,088,000 percent. The number of people 500 years of age or older has increased by 1,208,925,819,614,629,174,706,176,000 percent. The number of people 505 years of age or older has increased by 2,417,851,639,229,258,349,412,352,000 percent. The number of people 510 years of age or older has increased by 4,835,703,278,458,516,698,824,704,000 percent. The number of people 515 years of age or older has increased by 9,671,406,556,917,033,397,649,408,000 percent. The number of people 520 years of age or older has increased by 19,342,813,113,834,066,795,298,816,000 percent. The number of people 525 years of age or older has increased by 38,685,626,227,668,133,590,597,632,000 percent. The number of people 530 years of age or older has increased by 77,371,252,455,336,267,181,195,264,000 percent. The number of people 535 years of age or older has increased by 154,742,504,910,672,534,362,390,528,000 percent. The number of people 540 years of age or older has increased by 309,485,009,821,345,068,724,781,056,000 percent. The number of people 545 years of age or older has increased by 618,970,019,642,690,137,449,562,112,000 percent. The number of people 550 years of age or older has increased by 1,237,940,039,285,380,274,899,124,224,000 percent. The number of people 555 years of age or older has increased by 2,475,880,078,570,760,549,798,248,448,000 percent. The number of people 560 years of age or older has increased by 4,951,760,157,141,521,099,596,496,896,000 percent. The number of people 565 years of age or older has increased by 9,903,520,314,283,042,199,193,993,792,000 percent. The number of people 570 years of age or older has increased by 19,807,040,628,566,084,398,387,987,584,000 percent. The number of people 575 years of age or older has

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2000-01-01

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$$d(\mathcal{G}) = \frac{1}{n} \sum_{i=1}^n d_i = \frac{1}{n} \sum_{i=1}^n \sum_{j=1}^n A_{ij} = \frac{1}{n} \mathbf{1}^T \mathbf{A} \mathbf{1} = \frac{1}{n} \text{tr}(\mathbf{A} \mathbf{1} \mathbf{1}^T) = \frac{1}{n} \text{tr}(\mathbf{A} \mathbf{J})$$

1. *Phragmites australis* (Cav.) Trin. ex Steud.

[illegible]

*Journal of Management Education* 30(6)p.789-806

...and the

1. *Chlorophyll a* and *Chlorophyll b* were determined by the method of Arar and Collins (1971).

100

[illegible][illegible]

1. *Chlorophyll a* (Chl *a*)  
 2. *Chlorophyll b* (Chl *b*)  
 3. *Chlorophyll c* (Chl *c*)  
 4. *Chlorophyll d* (Chl *d*)  
 5. *Chlorophyll e* (Chl *e*)  
 6. *Chlorophyll f* (Chl *f*)  
 7. *Chlorophyll g* (Chl *g*)  
 8. *Chlorophyll h* (Chl *h*)  
 9. *Chlorophyll i* (Chl *i*)  
 10. *Chlorophyll j* (Chl *j*)  
 11. *Chlorophyll k* (Chl *k*)  
 12. *Chlorophyll l* (Chl *l*)  
 13. *Chlorophyll m* (Chl *m*)  
 14. *Chlorophyll n* (Chl *n*)  
 15. *Chlorophyll o* (Chl *o*)  
 16. *Chlorophyll p* (Chl *p*)  
 17. *Chlorophyll q* (Chl *q*)  
 18. *Chlorophyll r* (Chl *r*)  
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 20. *Chlorophyll t* (Chl *t*)  
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 22. *Chlorophyll v* (Chl *v*)  
 23. *Chlorophyll w* (Chl *w*)  
 24. *Chlorophyll x* (Chl *x*)  
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 26. *Chlorophyll z* (Chl *z*)  
 27. *Chlorophyll aa* (Chl *aa*)  
 28. *Chlorophyll ab* (Chl *ab*)  
 29. *Chlorophyll ac* (Chl *ac*)  
 30. *Chlorophyll ad* (Chl *ad*)  
 31. *Chlorophyll ae* (Chl *ae*)  
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 33. *Chlorophyll ag* (Chl *ag*)  
 34. *Chlorophyll ah* (Chl *ah*)  
 35. *Chlorophyll ai* (Chl *ai*)  
 36. *Chlorophyll aj* (Chl *aj*)  
 37. *Chlorophyll ak* (Chl *ak*)  
 38. *Chlorophyll al* (Chl *al*)  
 39. *Chlorophyll am* (Chl *am*)  
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 41. *Chlorophyll ao* (Chl *ao*)  
 42. *Chlorophyll ap* (Chl *ap*)  
 43. *Chlorophyll aq* (Chl *aq*)  
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 77. *Chlorophyll ayz* (Chl *ayz*)  
 78. *Chlorophyll azz* (Chl *azz*)  
 79. *Chlorophyll azaa* (Chl *aza*<sub>aa</sub>)  
 80. *Chlorophyll abz* (Chl *abz*)  
 81. *Chlorophyll acz* (Chl *acz*)  
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 96. *Chlorophyll arz* (Chl *arz*)  
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 107. *Chlorophyll acz* (Chl *acz*)  
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 129. *Chlorophyll ayz* (Chl *ayz*)  
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 131. *Chlorophyll azaa* (Chl *aza*<sub>aa</sub>)  
 132. *Chlorophyll abz* (Chl

*Journal of Management Studies*, 19(6), 701-718.

[illegible]

• **Prevalence** = the proportion of a population that has a disease at a particular point in time

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2.  $\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$  (the probability of getting heads on both coins)

1. *Chlorophyll a* and *Chlorophyll b* were determined by the method of Lichtenthaler and Whistler (1973).

1. *Chlorophyll a* and *Chlorophyll b* were determined by the method of Lichtenthaler and Whistler (1973).

1. În urma activității desfășurate în cadrul  
grupului de lucru, s-a constatat că activitatea  
de cercetare științifică este în curs de dezvoltare  
și că se realizează o colaborare între  
universități și instituții de cercetare.  
2. Activitatea de cercetare științifică este în curs  
de dezvoltare și se realizează o colaborare între  
universități și instituții de cercetare.  
3. Activitatea de cercetare științifică este în curs  
de dezvoltare și se realizează o colaborare între  
universități și instituții de cercetare.  
4. Activitatea de cercetare științifică este în curs  
de dezvoltare și se realizează o colaborare între  
universități și instituții de cercetare.  
5. Activitatea de cercetare științifică este în curs  
de dezvoltare și se realizează o colaborare între  
universități și instituții de cercetare.  
6. Activitatea de cercetare științifică este în curs  
de dezvoltare și se realizează o colaborare între  
universități și instituții de cercetare.  
7. Activitatea de cercetare științifică este în curs  
de dezvoltare și se realizează o colaborare între  
universități și instituții de cercetare.  
8. Activitatea de cercetare științifică este în curs  
de dezvoltare și se realizează o colaborare între  
universități și instituții de cercetare.  
9. Activitatea de cercetare științifică este în curs  
de dezvoltare și se realizează o colaborare între  
universități și instituții de cercetare.  
10. Activitatea de cercetare științifică este în curs  
de dezvoltare și se realizează o colaborare între  
universități și instituții de cercetare.

1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009, 2010, 2011, 2012, 2013, 2014, 2015, 2016, 2017, 2018, 2019, 2020, 2021, 2022, 2023, 2024, 2025, 2026, 2027, 2028, 2029, 2030, 2031, 2032, 2033, 2034, 2035, 2036, 2037, 2038, 2039, 2040, 2041, 2042, 2043, 2044, 2045, 2046, 2047, 2048, 2049, 2050, 2051, 2052, 2053, 2054, 2055, 2056, 2057, 2058, 2059, 2060, 2061, 2062, 2063, 2064, 2065, 2066, 2067, 2068, 2069, 2070, 2071, 2072, 2073, 2074, 2075, 2076, 2077, 2078, 2079, 2080, 2081, 2082, 2083, 2084, 2085, 2086, 2087, 2088, 2089, 2090, 2091, 2092, 2093, 2094, 2095, 2096, 2097, 2098, 2099, 2100, 2101, 2102, 2103, 2104, 2105, 2106, 2107, 2108, 2109, 2110, 2111, 2112, 2113, 2114, 2115, 2116, 2117, 2118, 2119, 2120, 2121, 2122, 2123, 2124, 2125, 2126, 2127, 2128, 2129, 2130, 2131, 2132, 2133, 2134, 2135, 2136, 2137, 2138, 2139, 2140, 2141, 2142, 2143, 2144, 2145, 2146, 2147, 2148, 2149, 2150, 2151, 2152, 2153, 2154, 2155, 2156, 2157, 2158, 2159, 2160, 2161, 2162, 2163, 2164, 2165, 2166, 2167, 2168, 2169, 2170, 2171, 2172, 2173, 2174, 2175, 2176, 2177, 2178, 2179, 2180, 2181, 2182, 2183, 2184, 2185, 2186, 2187, 2188, 2189, 2190, 2191, 2192, 2193, 2194, 2195, 2196, 2197, 2198, 2199, 2200, 2201, 2202, 2203, 2204, 2205, 2206, 2207, 2208, 2209, 2210, 2211, 2212, 2213, 2214, 2215, 2216, 2217, 2218, 2219, 2220, 2221, 2222, 2223, 2224, 2225, 2226, 2227, 2228, 2229, 2230, 2231, 2232, 2233, 2234, 2235, 2236, 2237, 2238, 2239, 2240, 2241, 2242, 2243, 2244, 2245, 2246, 2247, 2248, 2249, 2250, 2251, 2252, 2253, 2254, 2255, 2256, 2257, 2258, 2259, 2260, 2261, 2262, 2263, 2264, 2265, 2266, 2267, 2268, 2269, 2270, 2271, 2272, 2273, 2274, 2275, 2276, 2277, 2278, 2279, 2280, 2281, 2282, 2283, 2284, 2285, 2286, 2287, 2288, 2289, 2290, 2291, 2292, 2293, 2294, 2295, 2296, 2297, 2298, 2299, 2300, 2301, 2302, 2303, 2304, 2305, 2306, 2307, 2308, 2309, 2310, 2311, 2312, 2313, 2314, 2315, 2316, 2317, 2318, 2319, 2320, 2321, 2322, 2323, 2324, 2325, 2326, 2327, 2328, 2329, 2330, 2331, 2332, 2333, 2334, 2335, 2336, 2337, 2338, 2339, 2340, 2341, 2342, 2343, 2344, 2345, 2346, 2347, 2348, 2349, 2350, 2351, 2352, 2353, 2354, 2355, 2356, 2357, 2358, 2359, 2360, 2361, 2362, 2363, 2364, 2365, 2366, 2367, 2368, 2369, 2370, 2371, 2372, 2373, 2374, 2375, 2376, 2377, 2378, 2379, 2380, 2381, 2382, 2383, 2384, 2385, 2386, 2387, 2388, 2389, 2390, 2391, 2392, 2393, 2394, 2395, 2396, 2397, 2398, 2399, 2400, 2401, 2402, 2403, 2404, 2405, 2406, 2407, 2408, 2409, 2410, 2411, 2412, 2413, 2414, 2415, 2416, 2417, 2418, 2419, 2420, 2421, 2422, 2423, 2424, 2425, 2426, 2427, 2428, 2429, 2430, 2431, 2432, 2433, 2434, 2435, 2436, 2437, 2438, 2439, 2440, 2441, 2442, 2443, 2444, 2445, 2446, 2447, 2448, 2449, 2450, 2451, 2452, 2453, 2454, 2455, 2456, 2457, 2458, 2459, 2460, 2461, 2462, 2463, 2464, 2465, 2466, 2467, 2468, 2469, 2470, 2471, 2472, 2473, 2474, 2475, 2476, 2477, 2478, 2479, 2480, 2481, 2482, 2483, 2484, 2485, 2486, 2487, 2488, 2489, 2490, 2491, 2492, 2493, 2494, 2495, 2496, 2497, 2498, 2499, 2500, 2501, 2502, 2503, 2504, 2505, 2506, 2507, 2508, 2509, 2510, 2511, 2512, 2513, 2514, 2515, 2516, 2517, 2518, 2519, 2520, 2521, 2522, 2523, 2524, 2525, 2526, 2527, 2528, 2529, 2530, 2531, 2532, 2533, 2534, 2535, 2536, 2537, 2538, 2539, 2540, 2541, 2542, 2543, 2544, 2545, 2546, 2547, 2548, 2549, 2550, 2551, 2552, 2553, 2554, 2555, 2556, 2557, 2558, 2559, 2560, 2561, 2562, 2563, 2564, 2565, 2566, 2567, 2568, 2569, 2570, 2571, 2572, 2573, 2574, 2575, 2576, 2577, 2578, 2579, 2580, 2581, 2582, 2583, 2584, 2585, 2586, 2587, 2588, 2589, 2590, 2591, 2592, 2593, 2594, 2595, 2596, 2597, 2598, 2599, 2600, 2601, 2602, 2603, 2604, 2605, 2606, 2607, 2608, 2609, 2610, 2611, 2612, 2613, 2614, 2615, 2616, 2617, 2618, 2619, 2620, 2621, 2622, 2623, 2624, 2625, 2626, 2627, 2628, 2629, 2630, 2631, 2632, 2633, 2634, 2635, 2636, 2637, 2638, 2639, 2640, 2641, 2642, 2643, 2644, 2645, 2646, 2647, 2648, 2649, 2650, 2651, 2652, 2653, 2654, 2655, 2656, 2657, 2658, 2659, 2660, 2661, 2662, 2663, 2664, 2665, 2666, 2667, 2668, 2669, 2670, 2671, 2672, 2673, 2674, 2675, 2676, 2677, 26

These results suggest that the use of a single, non-validated questionnaire may not be sufficient to accurately measure the prevalence of mental health problems in the community. The use of a validated questionnaire, such as the GHQ-12, may be more appropriate for this purpose.